

HYDROGEN PRODUCTION BY WATER SPLITTING USING MIXED CONDUCTING MEMBRANES*

U. Balachandran, T. H. Lee, S. Wang, and S. E. Dorris
Energy Technology Division
Argonne National Laboratory
Argonne, IL 60439, USA

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ABSTRACT

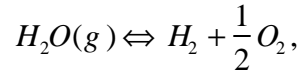
We have studied the production of hydrogen by water dissociation at moderate temperatures (700-900°C) with novel mixed-conducting membranes. Hydrogen production rates were investigated as a function of temperature, water partial pressure, membrane thickness, and oxygen chemical potential gradient across the membranes. The hydrogen production rate increased with both increasing moisture concentration and oxygen chemical potential gradient. A hydrogen production rate of 6 cm³(STP)/min-cm² was measured when we used a 0.10-mm-thick membrane at 900°C and 50 vol.% water vapor on one side of the membrane and 80% hydrogen (balance helium) on the other side. Hydrogen was used as a model gas on one side of the membrane to establish a high oxygen potential gradient; however, another reducing gas, methane, was substituted in one experiment to maintain the high oxygen potential gradient. The hydrogen production rate increased with decreasing membrane thickness, but surface kinetics played an important role as membrane thickness decreased.

INTRODUCTION

Hydrogen is considered the fuel of choice for both the electric power and transportation industries because of concerns over global climate change. At present, petroleum refining and the production of ammonia and methanol collectively consume ~95% of all deliberately manufactured hydrogen in the U.S., with petroleum refining accounting for ~70%. As crude oil quality deteriorates and restrictions on sulfur, nitrogen, and aromatic levels become increasingly stringent, hydrogen consumption by refineries will continue to increase. Most of the demands for hydrogen are currently met by fossil-based technologies such as steam reforming of natural gas, naphtha reforming (mainly in refineries), and coal gasification, all of which produce

greenhouse gases. Although considerable work is currently under way to improve existing hydrogen production technologies and to capture and store the greenhouse gases, interest in hydrogen production from renewable clean hydrogen resources is significant. In his 2003 State of the Union address [1], President Bush announced a FreedomFUEL Initiative that will develop hydrogen production and distribution technologies that are needed to power fuel cell vehicles and stationary fuel cell power sources. Currently, hydrogen is four times more expensive to produce than gasoline (when produced from its most affordable source, natural gas) [2]. The FreedomFUEL initiative seeks to lower that cost enough to make fuel cell cars cost-competitive with conventional gasoline-powered vehicles by 2010, and to advance the methods of producing hydrogen from renewable resources, nuclear energy, and coal [2]. There is particular interest in using water as a hydrogen source because it is clean and abundant, and the ability to efficiently produce hydrogen from water will dramatically improve America's energy security.

Water dissociates into oxygen and hydrogen at high temperatures:



but very low concentrations of hydrogen and oxygen are generated even at relatively high temperatures (e.g., 0.1 and 0.042% for hydrogen and oxygen, respectively, at 1600°C), because the equilibrium constant for this reaction is small [3]. However, significant amounts of hydrogen or oxygen can be generated at moderate temperatures if the equilibrium is shifted toward dissociation by removing either oxygen or hydrogen by using a mixed-conducting (electron- and ion-conducting) membrane. Although hydrogen can also be produced by high-temperature steam electrolysis, a mixed-conducting membrane offers the advantage that it requires no electric power or electrical circuitry. Hydrogen production with a mixed oxygen ion-electron conducting membrane is shown schematically in Fig. 1. The rate at which oxygen is removed from the water dissociation zone depends on the oxygen permeability of the membrane, which is a function of the electron and oxygen-ion conductivities, surface oxygen exchange kinetics of the membrane, and oxygen partial pressure (pO_2) gradient across the membrane [4-7]. Therefore, to obtain a high hydrogen production rate, membranes should exhibit high electron and oxygen-ion conductivities, good surface exchange properties, and be exposed to a high pO_2 gradient. Previous studies of hydrogen production by water dissociation with mixed-conducting

membranes showed only a modest hydrogen production rate above 1500°C, e.g., 0.6 cm³/min-cm² (STP) at 1683°C [8], mainly because of the low electronic conductivity of those membranes.

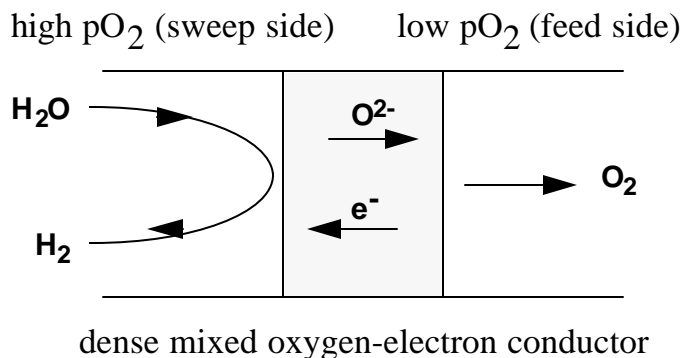


Fig. 1. Hydrogen production by water dissociation with a mixed oxygen ion-electron conducting ceramic membrane.

To increase the electronic conductivity of our membranes, we made a composite membrane that consisted of metal and oxygen-ion conducting ceramics (cermet membrane). In most of our studies of hydrogen production by water dissociation with these membranes, we used hydrogen as a model feed gas to obtain a high pO₂ gradient across the membrane. In one experiment, methane was used to establish the pO₂ gradient across the membrane, in which case hydrogen and syngas (mixture of hydrogen and carbon monoxide) were produced in the sweep (steam-side) and feed (oxygen-permeate side) gas, respectively. This paper presents the detailed results of hydrogen production by water dissociation with mixed-conducting cermet membranes.

EXPERIMENTAL

Acceptor-doped ceria (CMO) powder was obtained from Praxair Surface Technologies Specialty Ceramics. Cermet membranes were prepared from a mixture of CMO powder and a metal (40 vol.%) that has very low hydrogen permeability. Using a mortar and pestle, we prepared powder mixtures for the membranes in isopropyl alcohol. After evaporating the isopropyl alcohol, the dried powder was pressed into disks at 200 MPa and sintered for ~10 h at ~1400°C in a reducing atmosphere. To measure the hydrogen production rate, sintered disks were polished to the desired thickness with 600-grit SiC polishing paper. A polished disk was then affixed to an Al₂O₃ tube by using an assembly described elsewhere [9,10]. A gas-tight seal

formed when the assembly was heated to 900°C and spring-loaded rods squeezed a gold ring between the membrane and the Al₂O₃ tube. During sealing, 4% hydrogen/balance helium flowed over one side of the sample, while 100 ppm hydrogen/balance nitrogen flowed over the other side. For water splitting experiments, sweep gas (nitrogen that contained ~100 ppm hydrogen), bubbled through a water bath kept at various temperatures, was passed over one side of the sealed membrane. The temperature of the water bath controlled the water partial pressure (pH₂O) in the sweep side. A reducing gas (hydrogen-helium or methane-nitrogen-helium mixtures) was passed on the other side (feed side) to establish a pO₂ gradient across the membrane, which was maintained at 700-900°C. Using a thermal conductivity detector, we analyzed the gas concentrations in the sweep gas with an Agilent 6890 gas chromatograph (GC). The flow rates of both the sweep and feed gases were controlled with MKS mass flow controllers.

RESULTS AND DISCUSSION

The hydrogen production rate was measured as a function of pH₂O in the sweep gas. Measurements were made for membranes in the thickness range of ~0.3-1.0 mm at 900°C, in the pH₂O range from 0.03 atm (25°C water bath) to 0.49 atm (81°C water bath), with dry 80% H₂/balance He as the feed gas and 100 ppm H₂/balance N₂ as the sweep gas. Results of these measurements are shown in Fig. 2 for a 0.46-mm-thick membrane at 900°C. The hydrogen production rate increased from 1.2 to 2.4 cm³/min-cm² (STP) as the sweep pH₂O increased from 0.03 to 0.49 atm. For comparison, the hydrogen production rate was about two orders of magnitude lower when dry sweep gas was used, indicating that the high hydrogen production rate (1.2 to 2.4 cm³/min-cm²) is due to the dissociation of water. The hydrogen production rate showed a logarithmic dependence on pH₂O in the sweep gas. As the pH₂O in the sweep gas increases, the pO₂ increases, which increases the driving force for oxygen permeation from the sweep side (where the oxygen is produced through water dissociation) to the feed side (where the oxygen is consumed through reaction with hydrogen). Therefore, the hydrogen production rate increases as the pH₂O in the sweep gas increases. The logarithmic dependence of the hydrogen production rate on the pH₂O in the sweep gas is explained later in this paper.

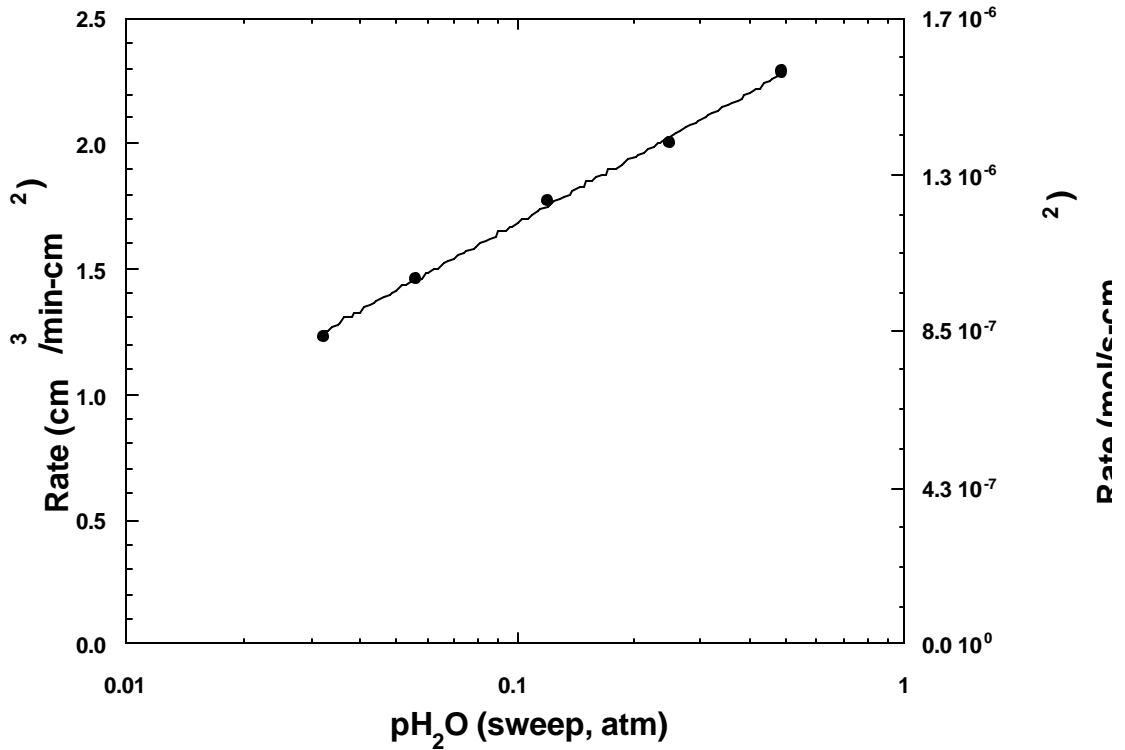


Fig. 2. Dependence of hydrogen production rate on p_{H_2O} in sweep gas. Membrane thickness = 0.46 mm; feed side p_{H_2} = 0.8 atm; temperature = 900°C.

The influence of feed side p_{H_2} on the hydrogen production rate is shown in Fig. 3. For these measurements, the p_{H_2O} in the sweep gas was 0.49 atm, and the membrane was 0.46 mm thick. Hydrogen concentration in the feed gas was controlled by mixing ultrahigh-purity (UHP) hydrogen and UHP helium with mass flow controllers. The hydrogen production rate increased with increasing p_{H_2} in the feed gas, showing a logarithmic dependence. As the hydrogen concentration in the feed gas increases, the p_{O_2} on the feed side decreases, thus increasing the driving force for oxygen permeation from the sweep to the feed side. Consequently, the hydrogen production rate on the sweep side increases as the p_{H_2} in the feed gas increases. In one experiment, 5% methane with a balance of nitrogen and helium was used as the feed gas. At 900°C, a hydrogen production rate of $\sim 0.3 \text{ cm}^3/\text{min-cm}^2$ (STP) was measured when the p_{H_2O} in the sweep gas was 0.49 atm. When compared with hydrogen, methane is much less reactive with the oxygen that diffuses through the membrane, especially in the absence of a reforming catalyst. Therefore, with methane in the feed gas rather than hydrogen, the p_{O_2} of the feed gas is higher and the p_{O_2} gradient across the membrane is lower. With the reduced p_{O_2} gradient, the removal

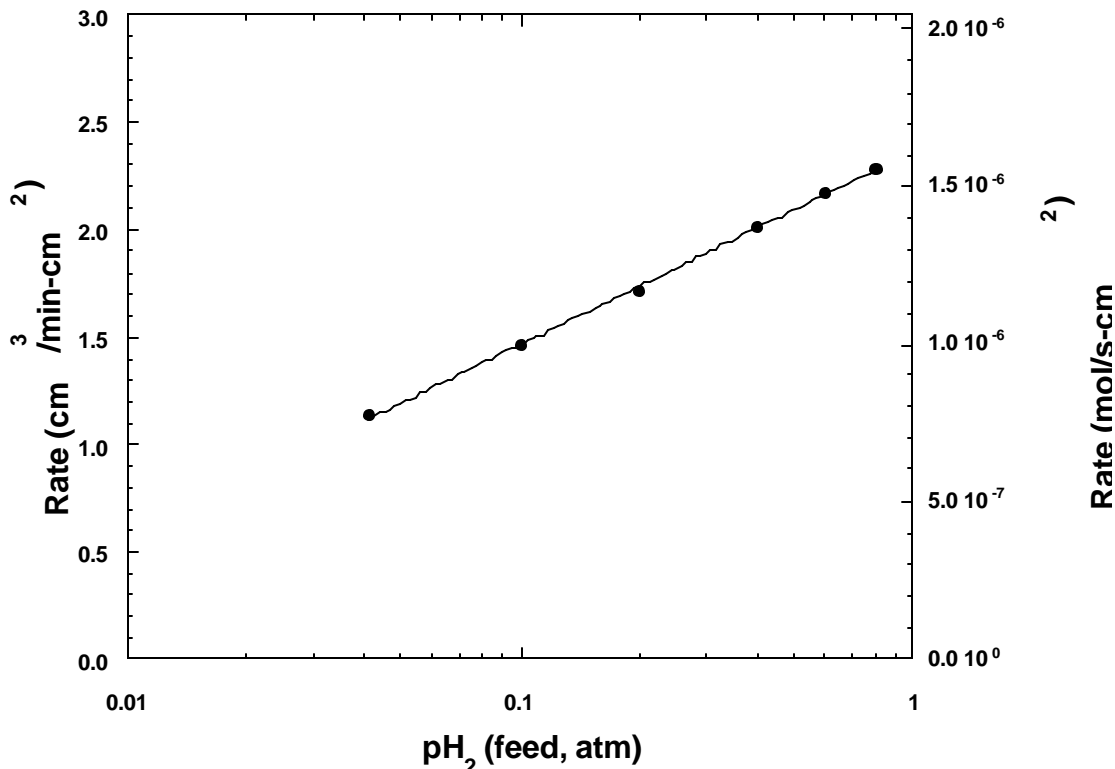


Fig. 3. Dependence of hydrogen production rate on p_{H_2} in feed gas. Membrane thickness = 0.46 mm; sweep p_{H_2O} = 0.49 atm; temperature = 900°C.

of oxygen from the sweep gas and the hydrogen production rate are decreased. Figure 4 shows the hydrogen production rate at 900°C as a function of p_{H_2O} in the sweep gas for a 0.46-mm-thick membrane with 5% methane as the feed gas. Due to limitations of our GC, we did not analyze the products on the feed side when methane was used as the feed gas, but we expect that syngas was produced.

The hydrogen production rate as a function of p_{O_2} gradient is shown in Fig. 5 for a 0.97-mm-thick membrane at 900°C. The p_{H_2O} in the sweep side was 0.49 atm. The feed gas was varied from 4% hydrogen to 80% hydrogen (balance helium). The p_{O_2} on the sweep side was estimated from the measured hydrogen concentration and the downstream concentration of H_2O (which is the difference between the initial and consumed H_2O concentration). The p_{O_2} on the feed side was estimated from the concentration of H_2O formed on the feed side and the concentration of downstream H_2 (which is the difference between the initial and consumed H_2 concentration). As can be seen in Fig. 5, the increase of the p_{H_2} in the feed gas corresponds to

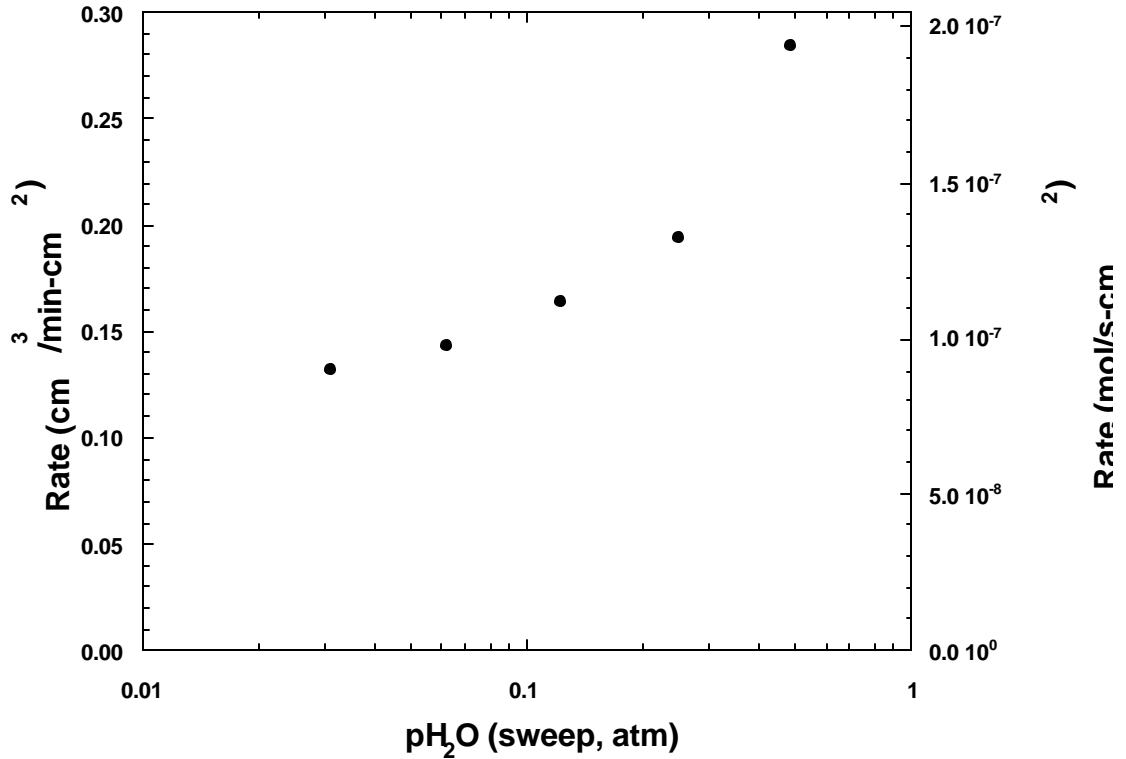


Fig. 4. Hydrogen production rate vs. p_{H_2O} in sweep gas for 0.46-mm-thick membrane. Feed gas = 5% methane/balance nitrogen and helium; temperature = 900°C.

the increase of p_{O_2} gradient, and the hydrogen production rate shows a logarithmic dependence on this p_{O_2} gradient. A similar result was also observed for the dependence of hydrogen production rate on the sweep p_{H_2O} (Fig. 2): the p_{H_2O} increase in the sweep gas corresponds to an increase of the p_{O_2} gradient. These results show that the hydrogen production rate is dependent on the p_{O_2} gradient across the membrane. In mixed oxygen ion-electron conductors, the logarithmic dependence of oxygen permeation rate on the p_{O_2} gradient is taken as evidence for a process that is limited by the bulk diffusion of oxygen [4-7, 11]. Notice that the hydrogen production from water dissociation is a direct result of oxygen removal, or oxygen permeation, from the sweep side. Therefore, the hydrogen production rate for the membranes that we have investigated is mainly limited by bulk oxygen diffusion under the measured conditions. However, surface kinetics will play an important role as the membrane thickness decreases.

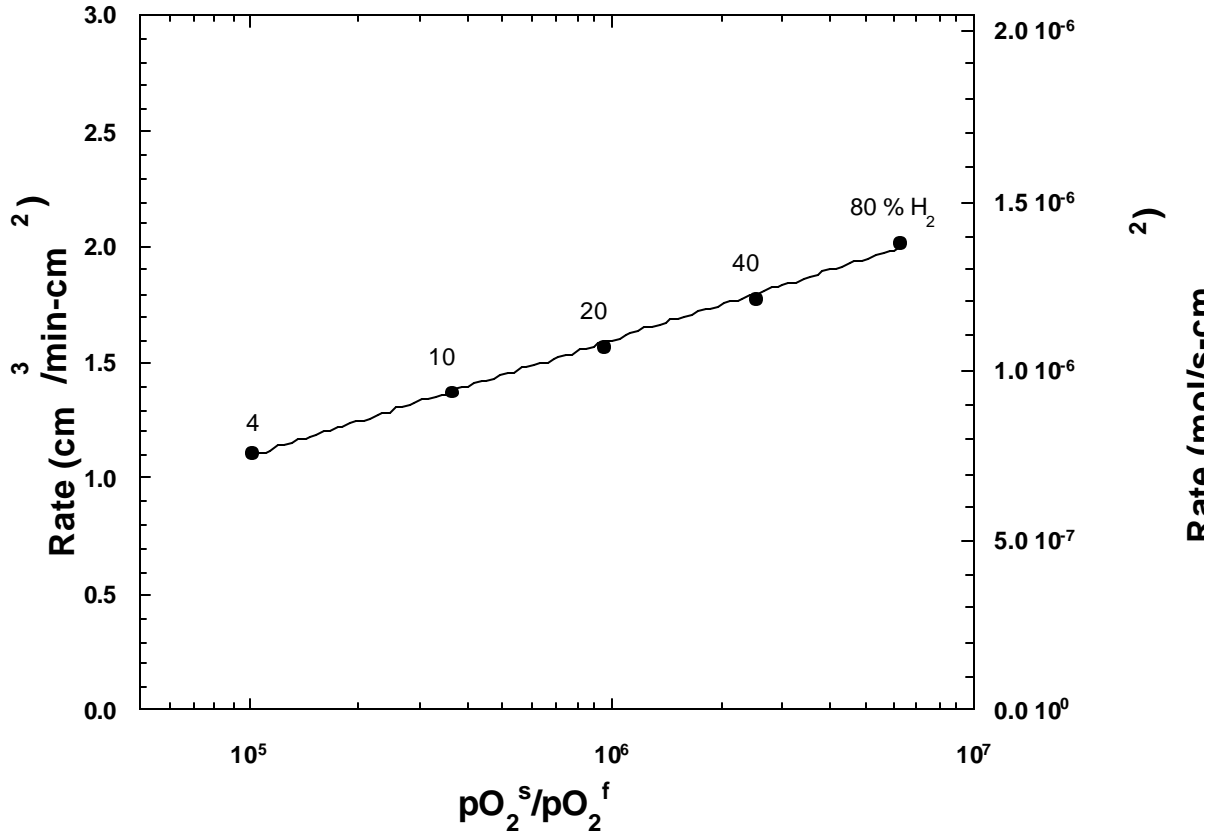


Fig. 5. Dependence of hydrogen production rate on pO_2 gradient across membrane. pO_2^s and pO_2^f are estimated sweep and feed pO_2 , respectively. Membrane thickness = 0.97 mm; temperature = 900°C.

The temperature and thickness dependence of hydrogen production rate were measured with $pH_2 = 0.8$ atm in the feed gas and $pH_2O = 0.49$ atm in the sweep gas. The hydrogen production rate was measured between 700 and 900°C at constant sweep and feed gas flow rates. The hydrogen production rates of four membranes (0.97, 0.46, 0.28, and 0.13 mm thick) are shown in Fig. 6. as a function of inverse temperature. The production rate increased with temperature and showed Arrhenius-type behavior, with an average apparent activation energy of 0.85 eV. A production rate of $\sim 1.5 \text{ cm}^3/\text{min-cm}^2$ (STP) was obtained at 750°C for a 0.13-mm thick membrane. The hydrogen production rate increased with decreasing membrane thickness, but the rate of increase declined as the membrane thickness decreased. Surface kinetics become important as the membrane thickness decreases below ~ 0.5 mm; with thin (~ 0.1 mm) membranes, they dominate hydrogen production. As seen from Fig. 6, a maximum production rate of $\sim 4 \text{ cm}^3(\text{STP})/\text{min-cm}^2$ was obtained with a 0.13-mm-thick membrane. To increase the

hydrogen production rate further, surface kinetics must be enhanced, which can be done either by increasing the surface area of the membrane [12,13] or by applying an active catalyst to the surfaces of the membrane [14].

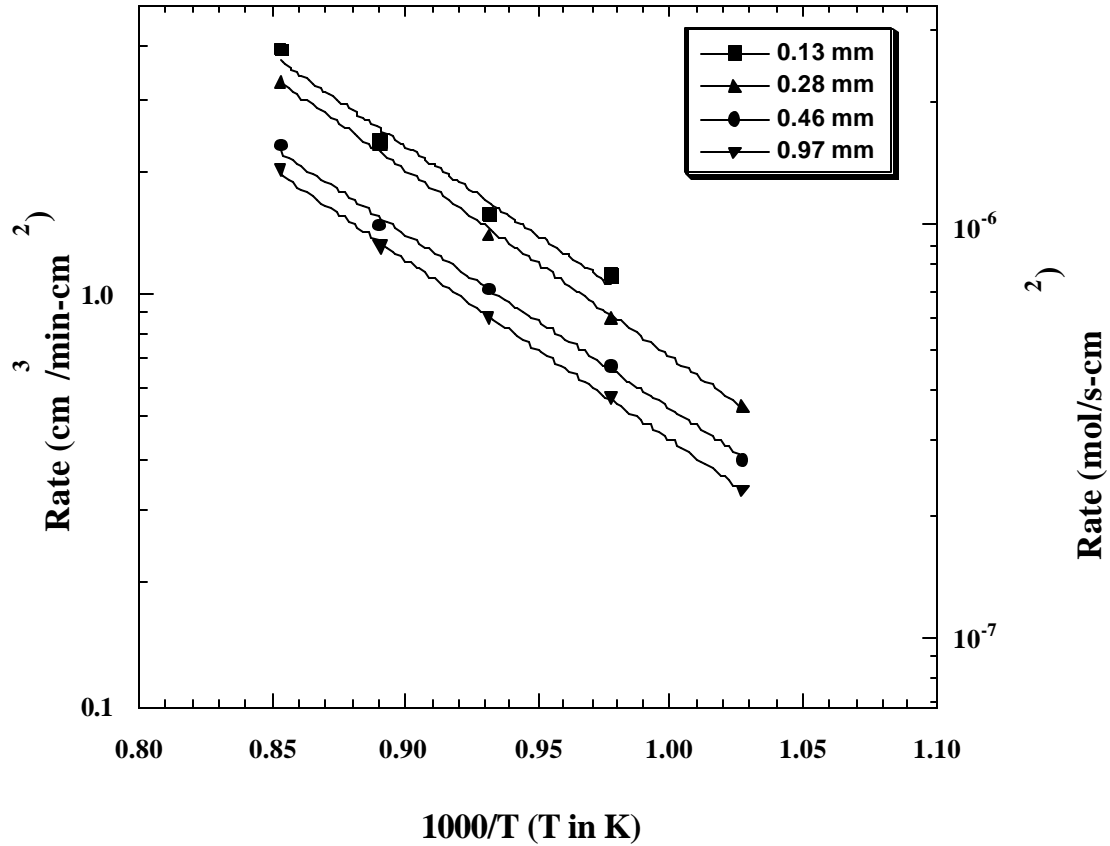


Fig. 6. Dependence of hydrogen production rate on temperature, with $p_{H_2} = 0.8$ atm in feed and $p_{H_2O} = 0.49$ atm in sweep. Membrane thicknesses are indicated on inset.

In an effort to enhance the surface kinetics and thereby increase the hydrogen production rate, we increased the surface area by applying porous cermet layers on both sides of a dense membrane. Figure 7 displays the hydrogen production rates for membranes with and without porous layers. Measurements were made at 900°C with 80% H_2 /balance He as the feed gas and 49% H_2O /balance N_2 as the sweep gas. As shown in Fig. 7, the porous layers significantly increased the hydrogen production rate. The maximum hydrogen production rate for a 0.13-mm-thick membrane modified with porous layers was $6.0 \text{ cm}^3 \text{ (STP)/min-cm}^2$. When compared with that of unmodified membranes, the hydrogen production rate of membranes with porous layers

increases more rapidly as the membrane thickness decreases because the hydrogen production rate, which is directly related to the permeation of oxygen through the membrane, is mainly determined by the surface oxygen exchange rate as the membrane thickness decreases. The nonlinear increase in hydrogen production rate with the inverse of membrane thickness indicates that the hydrogen production is still largely determined by surface reactions, even for surface-modified membranes. Thus, there is hope that other methods to enhance the surface kinetics may further increase the hydrogen production rates of these membranes.

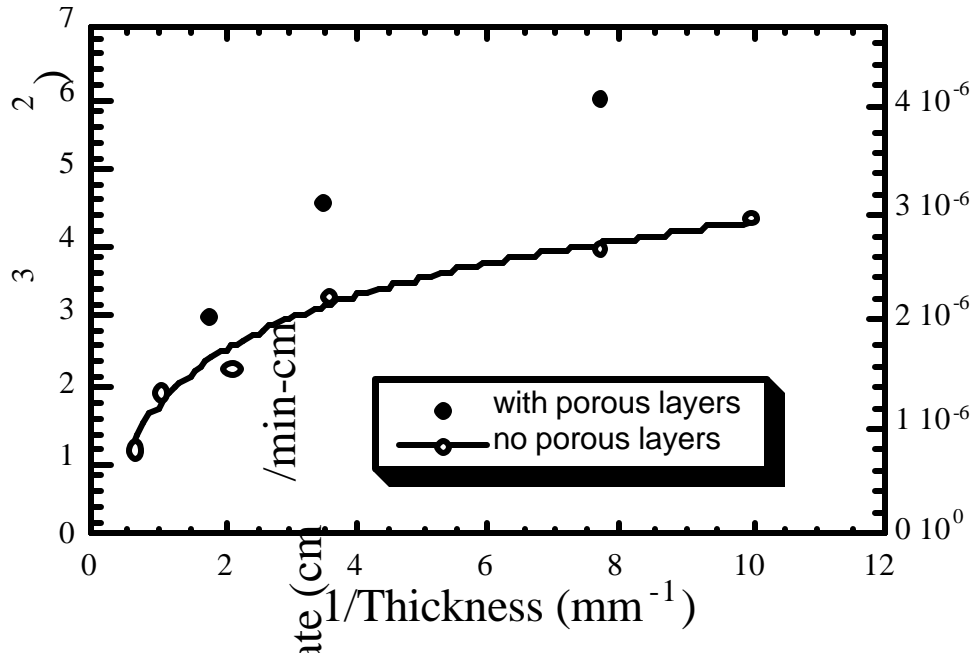


Fig. 7. Hydrogen production rates vs. inverse of membrane thickness of membranes with and without porous layers.

CONCLUSIONS

Mixed oxygen ion-electron conducting cermet membranes were developed to produce hydrogen through water dissociation at moderate temperatures (700-900°C). A maximum hydrogen production rate of 6.0 cm³ (STP)/min-cm² was obtained with a surface-modified, 0.13-mm-thick membrane. Because of the increased driving force for oxygen permeation from the sweep to the feed side, the hydrogen production rate increased with the p_{H₂O} in the sweep gas and with the p_{H₂} in the feed gas. The hydrogen production rate also increased with decreasing membrane thickness, but surface kinetics played an important role as the membrane thickness

decreased. Our results show that the hydrogen production rates may be increased further by enhancing the surface exchange kinetics either by increasing the active surface area of the membrane or by applying a water-dissociation catalyst to the surface of the membrane.

ACKNOWLEDGMENT

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REFERENCES

1. President Bush, State of the Union address to the Joint Session of Congress, Jan. 28, 2003.
2. U.S. Department of Energy, Energy Efficiency and Renewable Energy, FreedomFUEL web site <http://www.eere.energy.gov/freedomfuel/>
3. S. Ihara, Bull. Electrotech. Lab., **41**, 259, 1977.
4. B. Ma, U. Balachandran, C.C. Chao, J. H. Park, C. U. Segre, Ceram. Trans., **73**, 169, 1997.
5. P. S. Maiya, U. Balachandran, J. T. Dusek, R. L. Mieville, M. S. Kleefisch, and C. A. Udovich, Solid State Ionics, **99**, 1, 1997.
6. L. Qiu, T. H. Lee, L. M. Liu, Y. L. Yang, and A. J. Jacobson, Solid State Ionics, **76**, 321, 1995.
7. T. H. Lee, Y. L. Yang, A. J. Jacobson, B. Abeles, and M. Zhou, Solid State Ionics, **100**, 77, 1997.
8. H. Naito and H. Arashi, Solid State ionics, **79**, 366, 1995.
9. U. Balachandran, T. H. Lee, G. Zhong, S. E. Dorris, K. S. Rothenberger, B. H. Howard, B. Morreale, A. V. Cugini, R. V. Siriwardane, J. A. Poston Jr., and E. P. Fisher, in Studies in Surface Science and Catalysis, Ed. by J. J. Spivey, E. Iglesia, and T. H. Fleisch, Elsevier Science B.V., Amsterdam, The Netherlands, 465, 2001.
10. U. Balachandran, T. H. Lee, S. Wang, G. Zhang, and S. E. Dorris, Proc. 27th Intl. Conf. on Coal Utilization and Fuel Systems, published by Coal Technology Association, Gaithersburg, MD, **27**, 1155, 2002.

11. H. J. M. Bouwmeester and A. J. Burggraaf, in *The CRC Handbook of Solid State Electrochemistry*, Ed. by P. J. Gellings and H. J. M. Bouwmeester, CRC Press, Inc., Boca Raton, FL, 481, 1997.
12. T. H. Lee, Y. L. Yang, A. J. Jacobson, B. Abeles, and S. Milner, *Solid State Ionics*, **100**, 87, 1997.
13. H. Deng, M. Zhou, and B. Abeles, *Solid State Ionics*, **74**, 75, 1994.
14. G. Zhang, S. E. Dorris, U. Balachandran, and M. Liu, *Electrochem. and Solid State Letters*, **5**, J5, 2002.